

The University of Chicago

Absorption Spectra of Nitrosylsulfuric Acid
and of the Complex Compounds of
Copper Sulfate and of Ferrous
Sulfate with Nitric Oxide

A DISSERTATION

SUBMITTED TO THE FACULTY OF THE OGDEN GRADUATE SCHOOL
OF SCIENCE IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

BY

ALBERT SALATHE

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ABSORPTION SPECTRA OF NITROSYLSULFURIC ACID AND OF THE COMPLEX COMPOUNDS OF COPPER SULFATE AND OF FERROUS SULFATE WITH NITRIC OXIDE.

In the argument with which Raschig supports his theory¹ of the chamber process for the manufacture of sulfuric acid, his view that nitrosylsulfuric acid is stable only in solutions containing more than 80% of sulfuric acid plays an important role. The evidence for this view lies in the production of the blue substance, considered by him to be nitrosulfonic acid ($\text{H}_2\text{S}-\text{NO}_2$), by reduction of nitrosylsulfuric acid with mercury (a reaction that takes place only in solutions containing more than 80% of sulfuric acid) and in the failure to obtain this blue substance by action of sulfur dioxide on nitrosylsulfuric acid in such solutions. The fact that mercury does not produce the blue color in the more dilute solutions is taken as evidence that these solutions contain no nitrosylsulfuric acid; the fact that sulfur dioxide gives rise to the blue color only in the more dilute solutions is believed to demonstrate that sulfur dioxide reacts only with nitrous acid and not with nitrosylsulfuric acid to yield nitrosulfonic acid, and that in the more dilute solutions all of the nitrosylsulfuric acid has been hydrolyzed to ni-

¹ Raschig, *Z. angew. Chem.*, **18**, 1281 (1905); *J. Soc. Chem. Ind.*, **30**, 166 (1911).

trous acid. Generally, however, the formation of the blue substance itself is not relied upon because it is too unstable. Addition of copper sulfate (or ferrous sulfate) which intensifies the color reaction is made use of on the assumption that the intense coloration produced under these conditions is due to the formation of a copper (or ferrous) salt of nitrosylsulfuric acid. Upon the basis of this evidence Raschig concludes that nitrosylsulfuric acid cannot exist in the presence of sulfuric acid of concentrations such as are found in the lead chambers and that therefore it cannot be an intermediate in the chamber process. After thus ruling out nitrosylsulfuric acid, he develops from other experimental evidence his theory that the formation of the blue "nitrosylsulfuric acid" is the important step in the reactions which finally result in the formation of sulfuric acid.

Raschig's views concerning the stability of nitrosylsulfuric acid have already received rather cogent criticism from two sources. Reynolds and Taylor² have shown that by evaporation of solutions of 60–80% sulfuric acid containing nitrites, crystals of nitrosylsulfuric acid can be obtained. They therefore conclude that the latter must be stable in these solutions. While the present work has confirmed their conclusions fully it was possible that their results might have been open to another interpretation and that further confirmation was desirable. In the second place, Manchot³ has called attention to the fact that the blue coloration produced when copper sulfate is used in the reactions described above and used by Raschig as a test for the presence of nitrosylsulfuric acid, might readily be due to the formation of the deep violet complex salt of copper sulfate and nitric oxide, a salt analogous to the similar well-known complex salt of ferrous sulfate and nitric oxide. If Manchot's contention is correct, Raschig's color reaction has no necessary bearing on the question of the presence or formation of nitrosylsulfuric acid. This phase of the problem will receive further consideration later.

In the first part of this paper there are reported the results of an investigation of the absorption spectra of nitrosylsulfuric acid dissolved in sulfuric acid of various concentrations. From the data obtained it is possible to conclude definitely that the nitrosylsulfuric acid is not completely hydrolyzed until the concentration of the sulfuric acid, used as solvent, has been lowered to 40% by addition of water. It therefore follows that Raschig's criticism of the older theory of the chamber process on the ground of instability of nitrosylsulfuric acid is unjustified. With his other arguments this paper does not deal, except that in the second part some preliminary data bearing on the nature of "nitrosylsulfuric acid" are presented.

The absorption spectra of the solutions were examined with a quartz spectrograph of high accuracy. A spark discharge between carbon electrodes impregnated with oxides

² Reynolds and Taylor, *J. Soc. Chem. Ind.*, **31**, 367 (1912).

³ Manchot, *Z. angew. Chem.*, **24**, 13 (1911).

of molybdenum and uranium served as the source of light.⁴ Time of exposure varied for different types of solution from 30 to 45 seconds except for some of the most opaque solutions for which 90 seconds or more were required.

The solutions were contained in cells such as described by Baly. The windows were of quartz. The bulb was placed as near the end of the outer tube as possible to allow entrance of an inlet tube carrying nitric oxide for the experiments to be described in Part II. In the experiments with nitric oxide, the neck of the bulb was fitted with a 2-holed stopper in order to make it possible to keep the solution continuously saturated with the gas. Rubber tubing, 37 mm. in diameter, such as is used with Gooch crucibles, was employed to join the inner and outer tubes in the usual way. This tubing was found to lose its elasticity on subjection to the action of acid mixtures containing 75% of sulfuric acid and upwards, but to be singularly live after having been subjected to the action of weaker acids for considerable periods of time. The quartz windows were joined to the glass by means of water glass. This, if properly applied, will hold against concd. and dil. sulfuric and nitric acids for hours. After each experiment, the cells were immersed in lukewarm water, and in about half an hour the cement had dissolved and both quartz and glass were then thoroughly cleaned and made transparent by immersion in very dilute hydrofluoric acid.

The curves for the spectra are plotted in the usual way, with oscillation frequencies⁵ as abscissas and logarithms of thickness in millimeters as ordinates. In many cases, however, no reference concentration is given because the concentration of the absorbing substance is not known. The usual method of procedure was followed in making the photographs: first a photograph of the scale was taken, then a photograph of the whole spectrum through the empty Baly tube, then photographs of the absorption spectra of the solution and, finally, another photograph of the thinner layers of the solution. In this way the possibility of contamination of the solutions by the cement or the rubber was tested and excluded. Blank tests with sulfuric acid alone confirmed this observation.

I. Absorption Spectra of Solutions of Nitrosylsulfuric Acid in Sulfuric Acid of Various Strengths

The nitrosylsulfuric acid was prepared by the method of Weber.⁶ Further details of the method of preparation will be found below in connection with a discussion of the effect of impurities on the spectra. A series of 0.1 *N* solutions was prepared by dissolving the solid nitrosylsulfuric acid in 95.6%, 88.1%, 80%, 70%, 60%, 50% and 39.6% sulfuric acid. Two solutions, one in 93.1% and the other in 74.3% sulfuric acid, which were 0.025 *N* with respect to nitrosylsulfuric acid were examined and are included in the figure with the 0.1 *N* solutions. Fig. 1 represents the spectra of all of these solutions, plotted in the usual way and referred to 0.1 *N* solutions as standard.

There are two striking phenomena exhibited in Fig. 1. In the first place there is the increased ultraviolet absorption, or shift of end absorption toward the visible, with decrease in concentration of sulfuric acid used as solvent. In the second place there is the appearance of an absorption band in the ultraviolet as the concentration of the sulfuric acid approaches

⁴ Uhler and Wood, *Carnegie Inst. Pub.*, 1907, 69.

⁵ Wave number per mm.

⁶ Weber, *J. prakt. Chem.*, [1] 97, 489 (1866).

40%. The incipency of the band is noticeable at 50%, while at 39.6% acid the band is well defined. The interpretation of these phenomena is that the end absorption is due to nitrosylsulfuric acid and that the spectrum with the absorption band is due to nitrous acid.

This interpretation is based on the following evidence. The spectrum of nitrites is known.⁷ Spectra of potassium nitrite in 39.6% sulfuric acid,

photographed by me, checked with those of aqueous solutions of alkali metal nitrites within the limits of experimental error and are identical with the spectrum of nitrosylsulfuric acid in 39.6% sulfuric acid. It follows, therefore, that in sulfuric acid of this concentration, nitrosylsulfuric acid is completely hydrolyzed to nitrous acid.

Inasmuch as the chemical evidence (slight bubbling and momentary appearance of blue color) showed that this hydrolysis occurs when the sulfuric acid is diluted to 60% while the spectra gave no evidence of nitrous acid at this concentration, it seems probable that the nitrosylsulfuric acid, still undecomposed, blots out the spectrum of the nitrous acid. The greater opacity of the former makes this suggestion a very reasonable one, but it was thought best, nevertheless, to prove its correctness experimentally. For this purpose

one Baly tube was filled with a solution of 0.1 *N* nitrosylsulfuric acid in 39.6% sulfuric acid. This solution gives the spectrum of nitrous

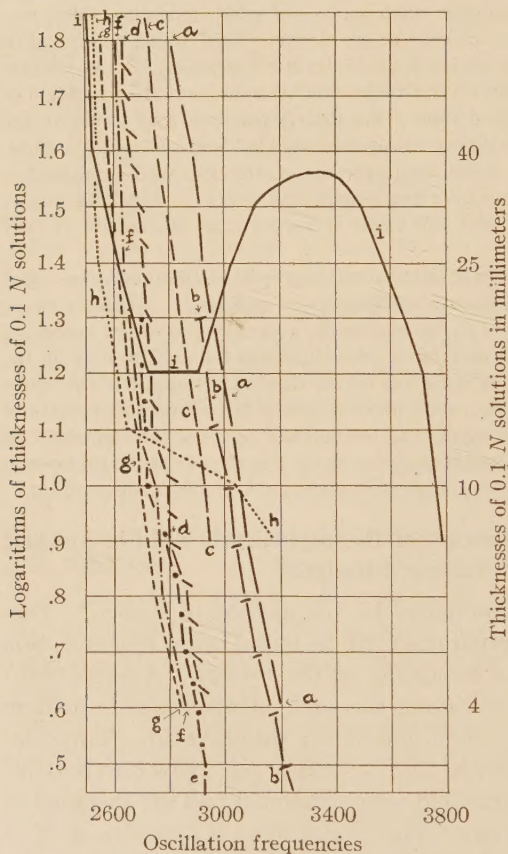


Fig. 1.—Absorption spectra of nitrosylsulfuric acid in sulfuric acid of various concentrations

a = 95.6%	d = 80.0%	g = 60%
b = 93.1%	e = 74.3%	h = 50%
c = 88.1%	f = 70.0%	i = 39.6%

⁷ Baly and Desch, *J. Chem. Soc.*, **93**, 1755 (1908). In this article the absorption spectrum of nitrosylsulfuric acid will also be found but for only one concentration of sulfuric acid. My data on nitrites are not reproduced in order to save space.

acid as was made clear above. This tube was preceded by another which contained, in one experiment, 0.1 *N* nitrosylsulfuric acid in 88.1% sulfuric acid and, in the second experiment, the same concentration of the solute in 80% sulfuric acid. Both of the solutions in the more concentrated acids exhibit the spectrum of the nitrosylsulfuric acid. In order to accommodate the two Baly tubes the source of light was placed 89 cm. from the slit and, to allow for the longer distances through which the light had to traverse the solutions, longer exposures were employed. In making the photographs, the length of the column of the solutions in the concentrated acids

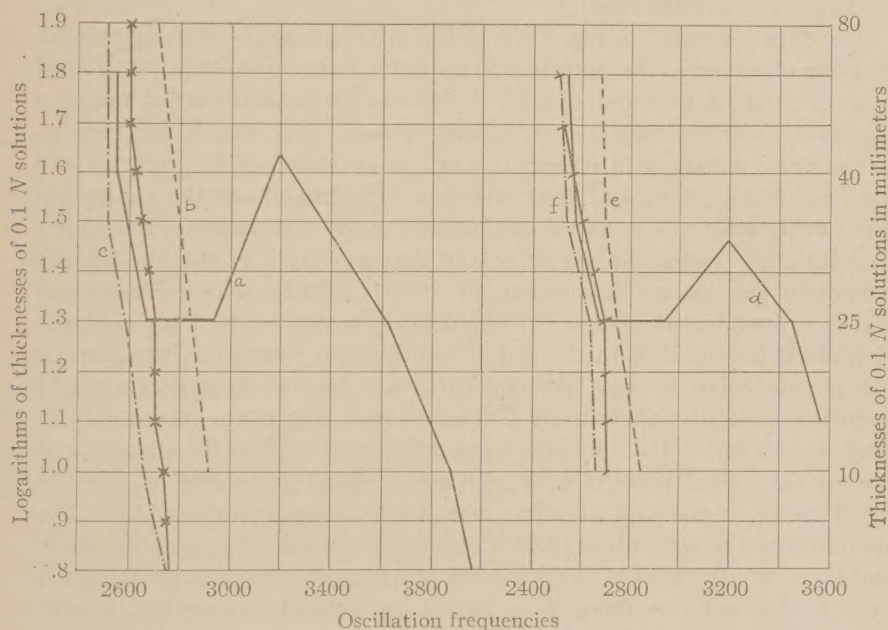


Fig. 2.— HSNO_3 dissolved in H_2SO_4 of strengths as follows:
 a = 39.6% b = 88.1% c = 39.6% and 88.1%
 d = 39.6% e = 80% f = 39.6% and 80%

was kept constant and the length of the solutions in the dilute acid was varied. If the assumption that the spectrum of the nitrosylsulfuric acid "blots" out that of the nitrous acid is correct, the resulting curves should be like those for a solution of nitrosylsulfuric acid in a concentration of sulfuric acid between 39.6% and that of the stronger acid used. If the decomposition of the nitrosylsulfuric acid is proportional to the decrease in concentration of the sulfuric acid this intermediate concentration of the latter should be the average of the strengths of the weaker and the stronger acids used in the experiment. While there is no reason to believe that this is necessarily the case, the curve for this average concentration is given in crossed lines with the curves for each of the solutions used and with

the curve of the superimposed spectra in Fig. 2. It is seen that while the spectrum of the acid of the average concentration is slightly different from that of the superimposed solutions, the similarity of the two is so great that there can be no doubt of the correctness of the assumption that the spectrum of nitrosylsulfuric acid masks that of nitrous acid. It follows from this that in solutions of sulfuric acid as dilute as 50% there is left undecomposed an appreciable quantity of nitrosylsulfuric acid. In so far as Raschig's criticism of the older theory of the chamber process is based upon his statement that nitrosylsulfuric acid cannot exist in the lead chambers, that criticism is unjustified.⁸

The data presented in Fig. 2 also aid in interpreting the shifting end absorption observed as the sulfuric acid is diluted from 96 to 60%. The most concentrated solution undoubtedly represents one in which little, if any, of the solute, nitrosylsulfuric acid, is decomposed. But, as the solution becomes more dilute (with respect to the concentration of the sulfuric acid used as solvent), more and more nitrous acid is formed and the absorption due to this substance is added to that due to the nitrosylsulfuric acid left in solution.⁹ Since the extent of the decomposition is not known, the curves for the spectra of solutions in sulfuric acid lying between 96 and 39.6% cannot be calculated. It is not likely, however, that the explanation given for the shift in the end absorption can completely account for the phenomenon, because the concentration of the nitrosylsulfuric acid decreases as that of the nitrous acid increases. The phenomenon may in part also be due to the influence exerted by the change in the character of the solvent. Similar shifts have been observed in other solutions, notably by Schaefer in the case of nitric acid dissolved in sulfuric acid.¹⁰ The similarity in the absorption spectra of nitrosylsulfuric acid, just described, and those of nitric acid in varying concentrations of sulfuric acid, described by Schaefer, is too striking to be passed by without comment. In both cases dilution of the sulfuric acid with water causes first a shift in the end absorption toward the visible, and then the gradual appearance of an absorption band. In both cases the band appears at approximately the same concentration.

It was at first thought that this striking similarity might be due to the presence of nitric acid in the nitrosylsulfuric acid. This was suspected al-

⁸ While qualitative spectroscopic evidence cannot lead to definite conclusions concerning the relative amounts of nitrosylsulfuric acid and of nitrous acid in these solutions, the fact that the shift in the end absorption is greater when the concentration of sulfuric acid is varied from 100 to 80% than when varied from 80 to 60% suggests that much of the decomposition of the nitrosylsulfuric acid occurs before the concentration of sulfuric acid has been lowered to 80%.

⁹ For the theory concerning the effect of two substances on the absorption spectrum of the resulting solution see, for example, Kayser, "Handbuch der Spektroskopie," S. Hirzel, Leipzig, 1905, vol. 3, p. 92.

¹⁰ Schaefer, *Z. anorg. Chem.*, **97**, 285; **98**, 77 (1916).

though the end absorption in the nitric acid and the band which develops as the water is added are both found much farther in the ultraviolet region than is the case with nitrosylsulfuric acid. To make sure that this difference in the region of absorption was not due to an error in the scale of wave lengths, either in Schaefer's work or in this, a plate of nitric acid in 39.6% sulfuric acid was made. The curve and Schaefer's agree well (See Fig. 3).

Error in scale is, therefore, excluded. In order to make sure that impurities played no role in the spectra of nitrosylsulfuric acid the following solutions were examined. In preparing the substance, the crystals were washed with glacial acetic acid and with carbon tetrachloride in order to dry them rapidly and free them from nitric acid. Examination of solutions of sulfuric acid to which a little carbon tetrachloride and glacial acetic acid had been added, showed that these impurities left the sulfuric acid transparent and that they could not have been responsible for the spectra. The fact that nitric acid is far more transparent than our solutions excludes it as the absorber. Finally, the fact that only nitrosylsulfuric acid could have been responsible for the absorption was demonstrated by photographing spectra of solutions prepared by (a)

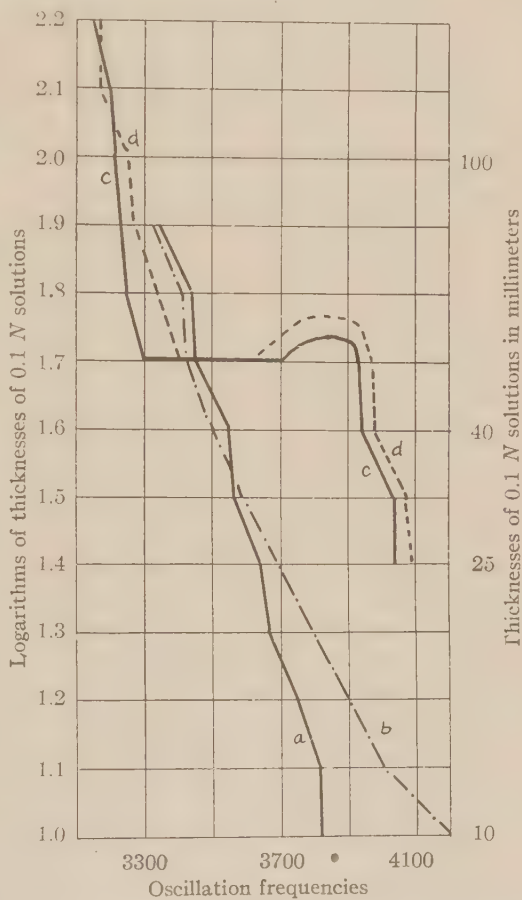


Fig. 3

a and b = HNO_3 in 88.1% H_2SO_4 ; a before, b after gently boiling for $\frac{1}{2}$ hour. c = KNO_3 in 39.6% H_2SO_4 , d = KNO_3 in 40% H_2SO_4 , after Schaefer

as described above, (b) dissolving pure sodium nitrite in concd. sulfuric acid, (c) dissolving, in sulfuric acid, nitrogen tetroxide prepared in one case by heating lead nitrate and in another by heating copper nitrate. All of these solutions gave absorption spectra which, except for unavoidable

differences in concentration, were identical. The curves are not reproduced in order to save space.

It has thus been shown that the great similarity between the absorption spectra of nitric and of nitrosylsulfuric acids in sulfuric acid of various strengths is not due to any common impurity. It is, therefore, probably due to a common cause, most probably the dehydrating action of sulfuric acid. In the case of the nitrous acid this action results in the formation of the mixed anhydride, nitrosylsulfuric acid. It is possible that with nitric acid a similar anhydride may be obtained or dehydration may proceed as far as nitrogen pentoxide.¹¹ The latter possibility suggests that a solution of nitric acid in concd. sulfuric acid might readily lose oxygen on account of the great instability of nitrogen pentoxide. If this occurs, nitrosylsulfuric acid must result. Lunge¹² states that this is the case and says further "this transformation takes place almost completely after brief boiling" for concentrations of acid of d. 1.71 (78.04%) and upwards. In the spectroscopic method we have a much more accurate means of testing the correctness of Lunge's statement than any means he used. A 0.1 *N* solution of nitric acid in 88.1% sulfuric acid was prepared and photographed. It was then gently boiled during half an hour open to the air and again photographed. Reference to Fig. 3 shows that very little if any nitrosylsulfuric acid was formed, for if it had been formed in even small amount absorption should have been greatly increased; as a matter of fact, the curves show slightly less absorption after boiling the acid, due, no doubt, to a small loss of nitric acid by evaporation. These findings were confirmed by chemical tests which, however, are not as sensitive as the spectra. While this result thus differs from the findings of Lunge, it is possible that the difference may be due to difference in concentration of the nitric acid.

One further suggestion in connection with our curves for nitrosylsulfuric acid is of interest. Since sulfuric acid is transparent in the range of frequencies examined, one might expect its mixed anhydride with nitrous acid to exhibit a spectrum similar to that of the latter.¹³ This is not the case; nitrous acid has an absorption band, nitrosylsulfuric acid only end absorption. This may indicate that in the latter there is an NO₂ group, since the evidence is fairly good that in nitrous acid the absorption spectrum is due to the ONO group. This point is not considered definitely proved; too little work on that type of isomerism in inorganic compounds, particularly with reference to absorption spectra, has as yet been done to warrant drawing definite conclusions.

¹¹ It is also possible that in the solutions in concd. acid a nitrate of sulfuric acid may exist. See Stieglitz, *J. Am. Chem. Soc.* **44**, 1293 (1922).

¹² Lunge, "Sulfuric Acid and Alkali," D. Van Nostrand Co., N. Y. **1913**, vol. I, part I, p. 343.

¹³ Simple anhydride formation usually does not greatly modify the absorption spectrum. See Hantzsch and Scharf, *Ber.*, **46**, 3570 (1913).

It may be added that the nitrosulfonic acid structure for nitrosylsulfuric acid has already received considerable attention.¹⁴

II. Absorption Spectra of the Complex Compounds of Ferrous and of Cupric Sulfate with Nitric Oxide. Comparison of these Spectra with that of Nitrosulfonic Acid.

As has already been mentioned, Manchot³ has pointed out that the intensely colored compounds produced by reduction of nitrosylsulfuric acid by mercury in the presence of ferrous or cupric sulfate might be complex salts of the type $\text{FeSO}_4\cdot\text{NO}$ instead of being nitrosulfonates as supposed by Raschig. A comparison of the spectra of solutions of the colored compounds prepared by reduction of nitrosylsulfuric acid with those of solutions prepared by passing nitric oxide into the sulfate solutions should afford a means of deciding this question and the necessary observations have, therefore, been made. The complex salts of nitric oxide have been studied in detail by Kohlschütter¹⁵ and by Manchot¹⁶ and their work, has shown that there are two classes of compounds of the same composition. In the case of ferrous sulfate, for example, a brown compound is formed when nitric oxide is passed into an aqueous solution of the salt while a deep red compound results from the action of nitric oxide on ferrous sulfate dissolved in concentrated solutions of sulfuric acid. For this reason it seemed necessary to study the absorption spectra of the ferrous sulfate-nitric oxide complexes in sulfuric acid of various strengths. It should be mentioned that Kohlschütter has already reported visual observations of these spectra, but these observations are not sufficiently precise to serve our purpose.¹⁷

The apparatus used in this part of the work was the same as that described in the first part of the paper. The nitric oxide was generated from copper pellets and nitric acid, diluted 1:1 with water. The gas was purified by passing it over soda lime, through concd. sodium hydroxide solution and then through concd. sulfuric acid. It is essential that the solutions in which the nitric oxide is absorbed be thoroughly freed from traces of oxygen, since the presence of the latter would give rise to the formation of either nitrosylsulfuric acid or of nitrous acid in the solutions. Each of these

¹⁴ See for example: Raschig, *Z. angew. Chem.*, **18**, 1281 (1905). Lunge, *ibid.*, **19**, 807, 857, 881 (1906). Gerard and Pabst, *Bull. soc. chim.*, [2] **30**, 531 (1878). Riehringers, "Chem. Techn. Unters.," 1917, p. 25.

¹⁵ Kohlschütter, *Ber.*, (a) **37**, 3044 (1904); (b) **40**, 873 (1907); (c) **44**, 1423 (1911).

¹⁶ Manchot, *Ann.*, (a) **350**, 368 (1906); (b) **375**, 308 (1910); (c) *Ber.*, **47**, 1601 (1914).

In the last named article a complete list of references to Manchot's work is given.

¹⁷ Before publication of this paper, Professor Kohlschütter was consulted in order to make certain that he would not consider this work an infringement of his field. He not only affirmed that this would not be the case but also most courteously put at my disposal some unpublished notes. I take great pleasure in acknowledging his kindness in this matter.

substances has an absorption spectrum that would interfere with the absorption spectra to be studied. To exclude oxygen, oxygen-free hydrogen was passed through the solutions until air had been completely removed and the solutions thereafter were not allowed to come into contact with any gas except hydrogen or nitric oxide.

Fig. 4 contains the curves for the compounds of ferrous sulfate and nitric oxide. The solutions were prepared by dissolving the salt in a little water and then adding enough diluted sulfuric acid to the mixture to produce the desired concentration of salt and of acid. After the air had been displaced

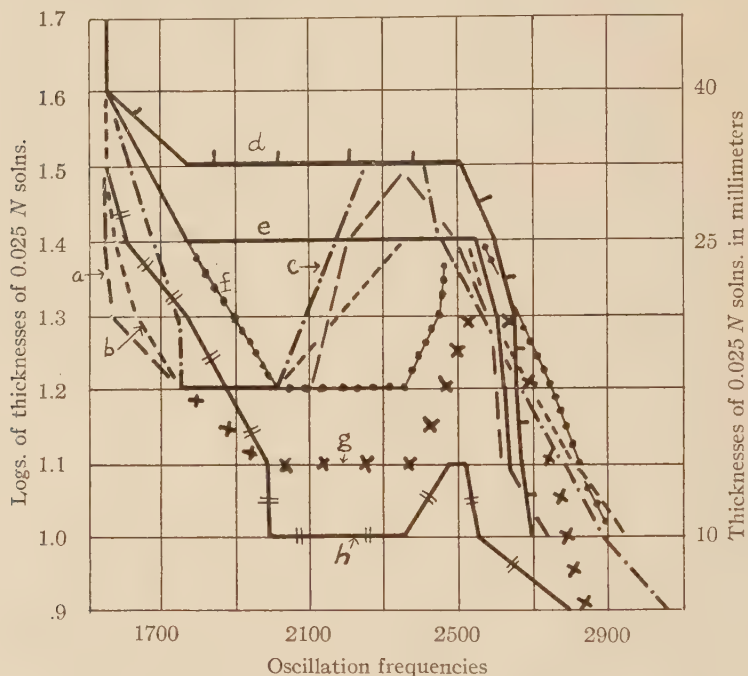


Fig. 4.—0.025 N FeSO_4 with NO in H_2SO_4 of following strengths:
 a = 93.1% b = 82.3% c = 71.5% d = 65.0%
 e = 59.4% f = 45.0% g = 15% h = 0%

from the solution by hydrogen, the solution was saturated with nitric oxide. The solutions represented by the curves of Fig. 4 were 0.025 N with respect to the iron salt; the strength of the acid was varied from 93.1% to 0%. The absorption spectra of the compound of nitric oxide with ferrous sulfate in 93.1, 82.3 and 71.5% sulfuric acid, respectively, all show an absorption band with head in the frequency interval from about 1750 to 2100; maximum transmission is approximately at 2300. These three curves, in other words, are very similar indicating that in this range of concentration of the sulfuric acid no change has occurred in the nature of the complex salt.

The curves for 65.0% and for 59.4% acid are quite different in character. The absorption band is no longer well defined and the region of absorption is much shallower. Further dilution produces still further change. With 45.0% acid there is again an absorption band, similar to the one just described, but its head is now in the frequency interval 2000 to 2400 and maximum transmission has been displaced to 2500. From this concentration of acid to solutions in water, the new absorption band remains unchanged except that it becomes deeper, that is, the solution becomes more opaque in the region of absorption. While the difference exhibited by these various curves is not very great, it is sufficiently definite and occurs at so definite a range of concentrations that it fully warrants the conclusion that there are two compounds, one existing in concd. sulfuric acid and the

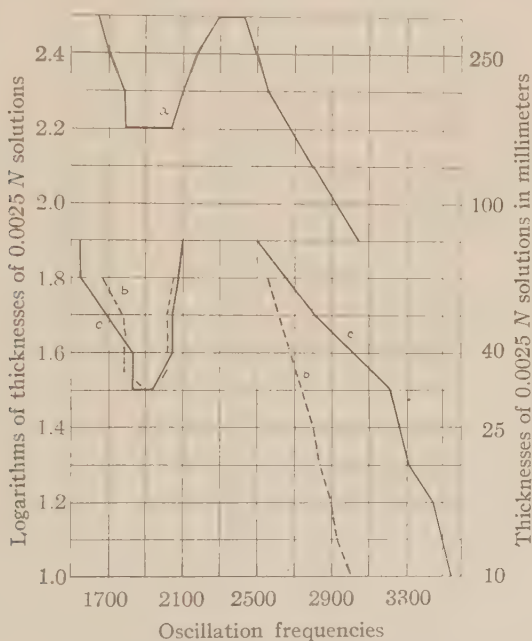


Fig. 5

a = 0.0025 N FeSO_4 with NO in 93.1% H_2SO_4 . b = ferrous nitrosulfonate in 93.1% H_2SO_4 ; Fe = 0.0025 N . c = 0.0025 N FeSO_4 with NO in 93.1% H_2SO_4

other in dilute acid or in water. As the concentration of the acid is changed from about 65% to about 50%, the one compound is transformed into the other. In the interval between these extremes, both compounds are apparently present and this fact causes the indefiniteness of the character of the curves for 65% and for 59.4% acid. These results corroborate the visual observations of Kohlschütter¹⁵ and the conclusions of Manchot¹⁶ based on chemical evidence but make much more precise the location of the

two bands and show, for the first time, the existence of the definite range of transition.¹⁸

Fig. 5 was made in order to show the identity of the compound of ferrous sulfate with nitric oxide, formed in concd. sulfuric acid, with Raschig's ferrous nitrosulfonate. The latter was prepared as follows. Ferrous sulfate was dissolved in water, sulfuric acid was added in sufficient amount to give a strength of 93.1%, and the mixture cooled. Sodium nitrite, finely

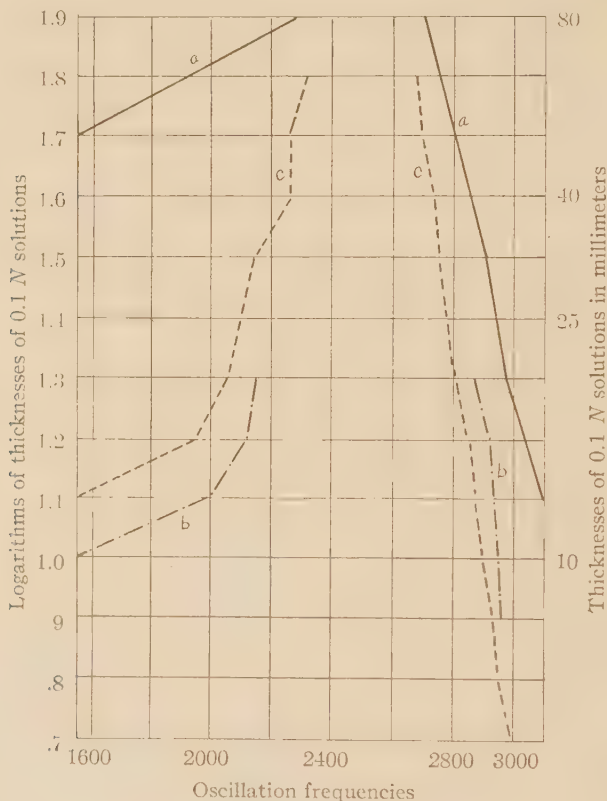


Fig. 6

a = 0.1 *N* CuSO₄ with NO in 82.3% H₂SO₄. b = 0.1 *N* CuSO₄ with NO in 93.1% H₂SO₄. c = Cu nitrosulfonate in 93.1% H₂SO₄; Cu = 0.1 *N*

ground and carefully dried, was then added slowly. The mixture was rotated until all of the particles of sodium nitrite had passed into solution. A few drops of mercury were added to this solution and the mixture was violently shaken for about 15 minutes. The characteristic red color developed and deepened during this interval. The concentration of the iron salt in this experiment was 0.0025 *N* and to make the comparison satisfac-

¹⁸ Kohlschütter (see Ref. 15 particularly 15c), gives a very well founded theory to account for the existence of these isomers. See also Manchot, Ref. 16c.

tory I prepared the iron compound, described in the preceding paragraph of this concentration also and photographed its spectrum. Curves b and c of Fig. 6 reproduce the experimental results. It is quite clear that Raschig's nitrosulfonate of ferrous iron and the complex compound of ferrous sulfate and nitric oxide formed in concd. sulfuric acid are identical.¹⁹

Fig. 6 shows that the compound obtained when nitric oxide is passed into copper sulfate dissolved in concd. sulfuric acid is identical with Raschig's nitrosulfonate of copper. The two compounds were prepared in quite analogous fashion as described for the respective iron salts. Both in the photographs of iron and of copper "nitrosulfonates," ultraviolet end absorption is superimposed on the spectra of the salts themselves. This is due to the fact that the method of preparation makes the exclusion of nitrogen tetroxide impossible. Furthermore, probably not all of the nitrosyl-sulfuric acid is reduced. This last fact also makes somewhat uncertain the concentration of the compound; all that can be given with accuracy is the concentration of the original metal salt.

The identity of the nitric oxide complexes with the supposed nitrosulfonates makes a study of the absorption spectrum of the latter of great interest. Baly and Desch⁷ report an observation on copper nitrosulfonate which agrees well with our data. Kohlschütter and Sazanoff²⁰ report a visual observation of the free acid which they find to have a spectrum quite different from that of the complex salts. My investigation by the more exact photographic procedure led to the opposite result as is shown in Fig. 7. Curve a represents the spectrum of nitrosulfonic acid prepared as described for its ferrous salt, except that no ferrous sulfate was added. The solution is very unstable and photography difficult.²¹ Owing to the impossibility of determining whether the reaction of the nitrite with mercury is complete or how much nitrosulfonic acid has decomposed, it is impossible to say what the concentration of the solution is. The nitrite was used in such concentration as to give a 0.5 *N* solution. Curve b represents another photograph of the spectrum of the copper salt. The concentration of the reagents here was only 0.1 *N* because of the greater opacity of the solution. Nevertheless, the actual data are recorded for both curves, since any attempt to recalculate them to a common basis of reference would have been quite arbitrary in view of the uncertainty concerning the concentrations.²² The two curves are seen to be closely similar.

¹⁹ Fig. 5 contains also the curve for FeSO_4NO in concd. sulfuric acid, but with an iron concentration 0.025 *N*. Both curves are referred to the concentration 0.0025 *N*. It is seen that Beer's law does not hold.

²⁰ Ref. 15c. More details are given in the dissertation by Sazanoff (Berne).

²¹ Exposures of 15 seconds were employed.

²² A second curve for "nitrosulfonic acid" is shown in "c" of Fig. 7. This solution was prepared by action of sodium sulfite on 0.5 *N* sodium nitrite dissolved in sulfuric acid in order to avoid the presence of mercury. Curves a and c agree well except for differences due to unavoidable differences of concentration.

Both show an absorption band with head at about 1900 and additional absorption (possibly a second incipient band) in the far red. Another striking point about these curves is that the absorption band is found in the same range of frequencies as is the absorption band for the compound which

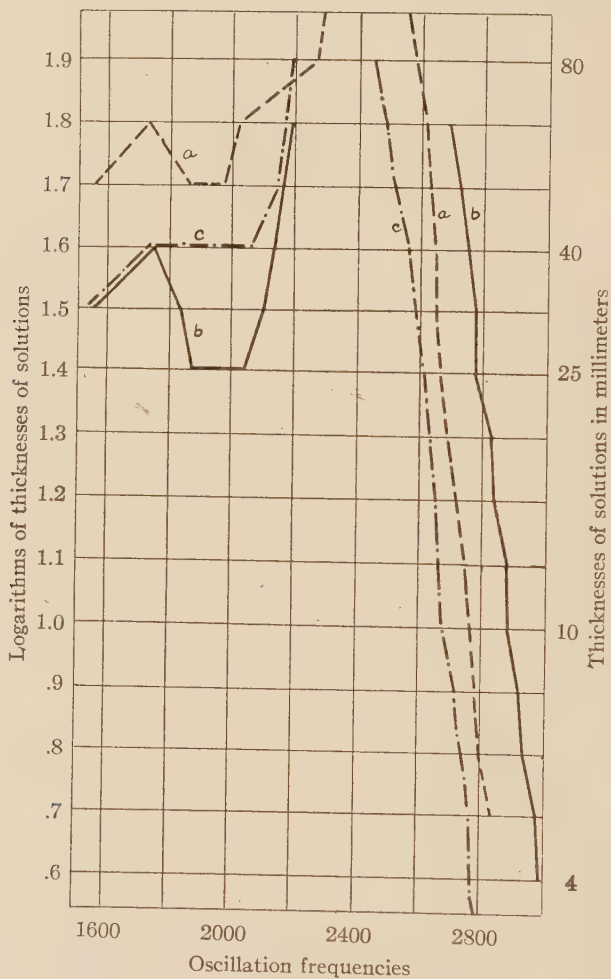


Fig. 7

a = nitrosulfonic acid from 0.5 *N* NaNO₂, H₂SO₄ and Hg. b = the Cu salt of a.
c = nitrosulfonic acid from 0.5 *N* NaNO₂, H₂SO₄ and Na₂SO₃

ferrous sulfate and nitric oxide form when mixed in the presence of concd. sulfuric acid.

This striking similarity suggests that "nitrosulfonic acid" is really a complex compound of sulfuric acid and nitric oxide whose formula might be written H₂SO₄.NO. According to this point of view, the supposed com-

plex has a very high dissociation pressure and can be formed only when nitric oxide is generated in contact with sulfuric acid so that there would be a high degree of supersaturation of the former. While Raschig has brought forward a number of experimental facts that tend to prove the correctness of his formulation for "nitrosisulfonic acid," practically all of them accord as well with the view here presented as with Raschig's. The fact that Manchot¹⁸ has been able to prepare a complex compound²³ of hydrogen chloride and nitric oxide, stable only at very low temperatures, favors the point of view here presented.²⁴ The spectroscopic evidence thus far available is not adequate, however, to decide this question definitely and more detailed discussion is, therefore, out of place.

In conclusion it gives me great pleasure to acknowledge to the Director of the Research Laboratory of the General Electric Company at Schenectady my sincere appreciation of his courtesy in granting me the use of a room and the facilities of the Laboratory for carrying out this research. I wish to include in this expression of appreciation all others of the staff of the Laboratory who most kindly aided me in securing apparatus and materials and in many other ways. I am deeply indebted to Professor Schlesinger, at whose suggestion and under whose direction the work was carried out.

Summary

1. The absorption spectra of nitrosylsulfuric acid dissolved in sulfuric acid of various concentrations have been obtained. The spectra show that appreciable quantities of the former remain undecomposed when the sulfuric acid is diluted with water to 50% and that, at higher concentrations of the latter acid, relatively large amounts of nitrosylsulfuric acid are present. This finding disproves one of the fundamental assumptions made by Raschig in developing his theory of the chamber process.

2. Absorption spectra of the complexes formed by ferrous sulfate with nitric oxide in solutions of sulfuric acid of various strengths have been photographed. The spectroscopic data confirm the view that there are two such complexes, both of the composition $\text{FeSO}_4 \cdot \text{NO}$, and show that one of them is stable when the sulfuric acid has a concentration above 65% and the other when the concentration of the acid is below 50%. Spectra of the complex, $\text{CuSO}_4 \cdot \text{NO}$, have also been obtained and the spectra of these complex salts have been compared with those of the so-called ferrous and cupric nitrosisulfonates and have been found to be identical.

3. A preliminary study of the absorption spectrum of "nitrosisulfonic acid" has shown it to be very similar to that of the ferrous sulfate-nitric

²³ Further information concerning this compound is found in the paper by Rodebusch and Yntema, *J. Am. Chem. Soc.*, **45**, 332 (1923).

²⁴ For a similar view, see Wentzki, *Z. angew. Chem.*, **24**, 392 (1911).

oxide complex existing in concd. sulfuric acid solution. This finding supports the view that possibly nitrosulfonic acid should be looked upon as an unstable solution of a complex compound of sulfuric acid and nitric oxide.

4. Examination of the spectra of solutions of nitric acid in concd. sulfuric acid, before and after heating the solutions, has shown that nitric acid is not readily decomposed in such solutions into nitrosylsulfuric acid, at least if the solution is not very concentrated with respect to nitric acid.

5. The character of the absorption spectrum of nitrosylsulfuric acid favors the view that this substance is present in solution largely as nitrosulfonic acid.

